A matrix matched reference material for validating petroleum Re-Os measurements

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Abstract

This study presents two matrix-matched reference materials developed for petroleum Re-Os measurements. We present the Re and Os mass fractions and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values (ratio of the number of atoms of the isotopes) for repeatedly measured aliquots (ca. 120 - 150 mg test portions) of the NIST Research Material 8505 (RM 8505) crude oil, and its asphaltene and maltene fractions, and ~ 90 g of homogeneous asphaltene powder isolated from this oil. Measurements were performed using the Carius Tube - Isotope Dilution - Negative Thermal Ionization Mass Spectrometry methodology. The RM 8505 crude oil contains 1.98 ± 0.07 ng g^{-1} Re and 25.0 ± 1.1 pg g^{-1} Os, with Re-Os isotope amount ratios of 452 ± 6 for $^{187}Re/^{188}Os$ and 1.51 ± 0.01 for $^{187}Os/^{188}Os$ (n = 20, 95% conf.). The homogeneous asphaltene sample contains 16.52 ± 0.10 ng g^{-1} Re and 166.0 ± 0.9 pg g^{-1} total Os, and possesses isotope amount ratios of 574 ± 3 for $^{187}Re/^{188}Os$ and 1.64 ± 0.01 for $^{187}Os/^{188}Os$ (n = 24, 95% conf.). The intermediate precision of these data makes the RM 8505 whole oil and the (~ 90 g) homogenised asphaltene appropriate petroleum matrix-matched reference materials for Re-Os measurements. The asphaltene fraction of the oil is the main carrier of Re and Os of the RM 8505 whole oil and caution is suggested in using asphaltene and maltene fractions of a single oil for Re-Os geochronology.

Key words: petroleum Re-Os measurements; reference material; N-TIMS; RM 8505 crude oil; homogenised asphaltene powder

1 Introduction

Since its inaugural application to the Polaris Mississippi Valley Type Pb-Zn deposit (Selby *et al.* 2005) and the Giant Oil Sands of Alberta, Canada (Selby and Creaser 2005), the rhenium-osmium (Re-Os) radioisotope system has been applied to many petroleum systems worldwide (Selby *et al.* 2007; Finlay *et al.* 2010; Finlay *et al.* 2011; Cumming *et al.* 2012; Finlay *et al.* 2012; Rooney *et al.* 2012; Lillis and Selby 2013; Cumming *et al.* 2014; Ge *et al.* 2016; Georgiev *et al.* 2016). These studies have demonstrated that the Re-Os isotope systematics of petroleum (crude oil, bitumen) allow the direct dating of the processes related to petroleum generation and evolution, and also provide insights into the source of the petroleum. Laboratory studies have also been carried out on the Re-Os isotope systematics of crude oil fractions (Selby *et al.* 2007; Mahdaoui *et al.* 2013; Mahdaoui *et al.* 2015; Georgiev *et al.* 2016). These studies have discussed the possible influences of geological processes on the Re-Os systematics of petroleum and its application to petroleum systems, e.g. the timing of oil generation, the precipitation of asphaltene, and the effect of contact with basinal fluids.

Previous Re-Os petroleum studies have utilized a wide range of sample types. They include not only conventional crude oil, but also the altered forms, e.g. bitumen of different origins. The Re-Os measurement methods were initially setup for rock samples, e.g. sulphides and organic-rich mudrocks (Cohen *et al.* 1999; Reisberg and Meisel 2002; Marques 2013; Zimmerman *et al.* 2014) and then adapted for the specific characteristics of petroleum

samples (Selby *et al.* 2005; Mahdaoui *et al.* 2013; Sen and Peucker-Ehrenbrink 2014; Georgiev *et al.* 2016). In general, current petroleum Re-Os measurement procedures adopt similar chemical purification procedures among different laboratories with the main differences being the digestion (i.e. choice of vessels and acids) and mass spectrometry (N-TIMS and ICP-MS) methods. The two noteworthy characteristics of petroleum samples that the protocols have to deal with are the low mass fractions (abundances) of Re ($\leq$1 ng g^{-1}) and Os (~ 10 pg g^{-1}) of many oils (see Selby *et al.* 2007) and the high pressure during the digestion.

Petroleum samples are usually digested in closed-system (Carius tubes and Anton Paar High Pressure Asher (HPA-S) vessels) with strong oxidizing acids. The digestion process should ensure the complete destruction of the organic matrix and the achievement of the highest oxidation state of all Os, i.e. OsO_4, to permit the equilibrium of the sample and spike Os. The most commonly used digestion reagent is concentrated nitric and hydrochloric acid in the form of inverse *aqua regia*. The addition of hydrogen peroxide is demonstrated to increase the efficiency of sample digestion and the mass spectrometer Os signal (Li *et al.* 2011). However, it also increases the risk of Carius tube rupture during digestion. The low Re and Os concentrations of many crude oils require a large amount of sample and low procedural blanks to obtain accurate and precise data. However, the high pressure generated by the formation of carbon dioxide during the digestion process limits the amount of sample that can be handled with the current digestion technique. The HPA-S method has been used to digest up to 0.45 g of crude oil effectively (Georgiev *et al.* 2016) and 1 g pumpkin seed oil (90 ml quartz vessel, Bandoniene *et al.* 2013) and it can also digest samples in short times (overnight or ~ 2-3 hrs). Further, a recent study described the design of re-useable Carius tubes (Qi *et al.* 2013). Both Carius tubes and HPA-S methods can yield low blanks, with the blanks primarily

controlled by the reagents used. Importantly, reuse of digestion vessels increase the probability of variable blanks, which can hamper the application of most appropriate blank correction. When tubes are not reused, the Carius tube - inverse aqua regia methodology typically yields low Re and Os blanks across different labs, e.g. generally lower than 10 pg for Re and 50 - 200 fg for Os (e.g. Cumming *et al.* 2014 and this study, Table 1), less than 3 pg Re and 2 pg Os (Steven *et al.* 2015), and 3.7 ± 4.7 pg Re and 340 ± 226 fg Os (Georgiev *et al.* 2016).

After sample digestion and spike-sample equilibration, the Os fractions are typically extracted with an organic solvent and purified by micro-distillation (Cohen and Waters 1996; Birck *et al.* 1997), with the Re fractions being purified by anion exchange chromatography (Morgan *et al.* 1991; Selby and Creaser 2001). The Re and Os isotope compositions of the purified Re and Os fractions from samples are determined by Negative Thermal Ionization Mass Spectrometry (N-TIMS) and/or (Multi-Collector) Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS/ICP-MS) (Creaser *et al.* 1991; Völkening *et al.* 1991; Reisberg and Meisel 2002; Meisel *et al.* 2003; Walczyk 2004; Nowell *et al.* 2008). The MC-ICP-MS/ICP-MS permits faster isotope ratio determination and simpler elemental purification chemistry. However, the N-TIMS methodology is a more appropriate reference technique for Os isotope ratio measurement because of its advantage of high ionisation efficiency, no significant memory and small mass fractionation which are especially important for oils that often possess low mass fractions of Os.

The pursuit of simple, rapid and low uncertainty Re-Os measurement of petroleum and the demand for both intra-laboratory calibration and inter-laboratory comparison are driven by the increasing interest and application of petroleum Re-Os measurement. Considering the

unique nature of petroleum samples, e.g. easy to digest, significant CO_2 generated during digestion and typically low Re and Os mass fractions, a matrix-matched reference material is needed for petroleum Re-Os measurement method development and validation. Some progress has already been made (Sen and Peucker-Ehrenbrink 2014). In this study, we present Re-Os data for the National Institute of Standards and Technology (NIST) vanadium Research Material 8505 crude oil and a homogeneous asphaltene sample (~ 90 g) isolated from the RM 8505 oil, to demonstrate their use as appropriate petroleum matrix-matched reference materials for Re-Os measurement. These two samples are repeatedly analysed for their Re and Os mass fractions and isotope ratios via the Carius Tube - Isotope Dilution - NTIMS methodology. In addition, based on the Re-Os analysis of individually separated asphaltene and maltene fractions in this study, we further confirm that asphaltene is the main carrier of Re and Os within crude oils, and that there is negligible Re and Os in the volatile fraction (at 80 °C) of this oil.

2 Samples preparation

Research Material 8505 is a Venezuelan crude oil with currently (year of 2017) approximately 100 bottles of 250 ml in stock which should last for more than ten years given current sales rate. This longevity estimate may reduce if the Research Material 8505 is adopted for more for research methods other than vanadium, as proposed here for Re-Os research. The oil was produced in 1983 and received from the Scallop Petroleum Company, a subsidiary of Royal Dutch Shell. No geological details concerning the origin of this oil are available. The predominant source rocks (95% source of Venezuelan's crude oil) of Venezuela are the Upper Cretaceous (Cenomanian-Turonian-Coniacian, 100 – 86 Ma) La Luna Formation and its age equivalents, with only minor contributions from Palaeocene,

Eocene and Miocene source rocks (James 1990 2000; Summa *et al.* 2003). Oil generation from the La Luna Formation is considered to have occurred from the Early Eocene onwards (≤ 56 Ma), with the majority of the oil having been generated since the Miocene (James 2000; Summa *et al.* 2003).

In this study, four sample types were repeatedly analysed for their Re and Os mass fractions and isotope (amount) ratios, i.e. the RM 8505 crude whole oil, the individually separated asphaltene and maltene fractions from RM 8505, and a homogenised asphaltene sample. Five bottles of RM 8505 crude oil were used and subtitled A, B, C, D and E.

The asphaltene fraction of an oil is defined as the insoluble fraction of oil in *n*-alkanes and the maltene is the soluble fraction. The separation in this study is done by adding 40 ml of *n*-heptane to ~ 1 g of whole oil (Speight 2004; Selby *et al.* 2007). The *n*-heptane and crude oil were thoroughly mixed and left on a rocker overnight at room temperature. The next day the mixture was centrifuged at 3500 rpm for 15 minutes. The precipitated asphaltene was separated by decanting the maltene-bearing *n*-heptane. The asphaltene fraction was transferred to a glass vial using chloroform and dried at 60 °C. The maltene fractions were recovered by evaporating the *n*-heptane at 80 °C in a glass vial.

To produce the homogenised asphaltene powder, the asphaltene fraction of ~ 1 kg of RM 8505 oil from all five bottles was isolated and homogenised. The isolation procedure of the asphaltene was generally the same as the *n*-heptane method described above. The difference is that the *n*-heptane asphaltene-maltene mixture was filtered through 0.45 µm Whatman glass microfibre filter instead of being centrifuged. The dried asphaltene was ground to fine powder (< 212 µm) using an agate pestle and mortar, homogenised, and then evenly

distributed into 12 glass bottles with 7.5 g of asphaltene placed into each bottle. This amount asphaltene will permit 50 analyses if using 150 mg aliquots per Re-Os analysis. All of the 12 glass vials are retained at Durham University and can be obtained via David Selby, which is expected to last for five to ten years. The asphaltene accounts for ~ 11% of the whole oil. For the bulk separated asphaltene, the maltene was not recovered from *n*-heptane or measured for Re-Os.

For bottle A, six Re-Os analyses on each of the whole oil, individually separated asphaltene and maltene fractions were conducted. For bottles B, C, D, and E, three Re-Os analyses were carried out for each of the three sample types from every bottle. The asphaltene and maltene samples represent paired petroleum fractions from the separation of ~ 1 g crude oil by *n*-heptane. They are not separated from the whole oil Re-Os analysis samples from the same bottle. In total we present the data of eighteen Re-Os analyses of each sample type for the five bottles. In addition, Re-Os analyses were performed on two samples taken from each of the twelve bottles of the homogenised asphaltene powder.

3 Measurement procedure

The Re and Os mass fractions and Re-Os isotopic systematics were determined by the Isotope Dilution – Negative Thermal Ionisation Mass Spectrometry (ID-NTIMS) method at Durham University in the Laboratory for Source Rock and Sulphide Geochronology and Geochemistry (a member of the Durham Geochemistry Centre). The analytical protocols are based on those developed in previous studies (Creaser *et al.* 1991; Shirey and Walker 1995; Birck *et al.* 1997; Selby and Creaser 2001; Selby *et al.* 2007).

The sample test portion sizes used for each Re-Os analysis were ~ 150 mg of whole oil and maltene, ~ 120 mg of the individually separated asphaltene and ~ 150 mg for the homogenised asphaltene powder. The solid asphaltenes were weighed using weighing paper. The viscous crude oil and maltene were weighed in small glass vials (~ 3 ml and 4.5 g) and then transferred into a pre-cleaned (with step 1 by 5% H_2O_2, step 2 by 8 mol l^{-1} HNO_3, step 3 by high purity water) Carius tubes with the aid of ~ 1 ml chloroform, which was evaporated at 60˚C.

After adding a known amount of ^{185}Re + ^{190}Os mixed tracer solution, the samples were dissolved and equilibrated in Carius tubes using inverse *aqua regia* (3 ml 12 mol l^{-1} HCl + 6 ml 16 mol l^{-1} HNO_3) at 220 °C for 24 hrs. A solvent extraction methodology was used to isolate the Os from the digested solution using 3 x 3 ml aliquots of chloroform. The Os was then back-extracted from chloroform with 3 ml 9 mol l^{-1} HBr solution at room temperature on an analogue rocker overnight. Then separated HBr solution was evaporated to dryness, with the remaining Os fraction further purified by micro-distillation using the CrO_3-H_2SO_4-HBr technique. The purified Os fraction was loaded onto Pt wire filament and covered with ~ 0.3 µl of NaOH-$Ba(OH)_2$ activator solution (6 mg NaOH with 20 mg $Ba(OH)_2$ in 1 g of ultrapure H_2O) (Selby and Creaser 2001; Luguet et al., 2008). Following the extraction of Os, the acid medium was evaporated to dryness with the Re fraction purified by anion exchange chromatography. The eluted solution containing Re was evaporated to dryness and the Re was loaded onto a Ni wire filament with ~ 0.5 µl saturated $Ba(NO_3)_2$ in ultrapure H_2O activator solution (Creaser *et al.* 1991). The Re and Os isotope ratio measurements were conducted on a Thermo Scientific TRITON mass spectrometer via ion-counting using a secondary electron multiplier in peak-hopping mode for all Os and maltene Re, and static Faraday collection for oil and asphaltene Re. The measured oxide ion ratios for Os and Re

were corrected for isobaric oxygen interferences to obtain element ratios, which were then corrected for mass fractionation using a $^{192}Os/^{188}Os$ value of 3.08761 (Nier 1937) and a $^{185}Re/^{187}Re$ value of 0.59738 (Gramlich *et al.* 1973), spike contributions and blank. The total procedural blanks during the study are 1.90 ± 0.97 picograms for Re and 73 ± 19 femtograms for Os, with an average $^{187}Os/^{188}Os$ of 0.24 ± 0.03 (internal error weighted average by *Isoplot*, 95% conf., n = 7; Table 1). An in-house Os control solution, DROsS, yields an average $^{187}Os/^{188}Os$ of 0.1611 ± 0.0008 (2 *s*, *n* = 126) being identical to the reference value of 0.160924 ± 0.000004 (2 *s*, Luguet *et al.* 2008; Nowell et al., 2008; Cumming et al., 2014 and references therein). The in-house Re reference solution yields an average $^{185}Re/^{187}Re$ of 0.5989 ± 0.0003 (*n* = 116, 95% conf.) which is used for the correction of mass fractionation in comparison with the accepted $^{185}Re/^{187}Re$ value of 0.5974 (Gramlich *et al.* 1973). For each sample the final expanded (k = 2) combined standard uncertainties presented for the Re and Os data (Tables 2 - 5) were calculated by full propagation of uncertainties in weighing, blank correction and spike calibrations, mass spectrometry measurements of Re and Os, and the intermediate precision of the results of repeated measurements of Re and Os reference solution. Additionally we also present the error correlation value (rho) between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ for these samples (Cumming 1969; Ludwig 1980; Schmitz and Schoene 2007).

4 Results and discussion

The Re and Os mass fractions and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values are presented in Tables 2 - 5 and Figure 1 - 5. For the entire Re-Os data set for each sample type (e.g., whole oil, asphaltene, maltene, homogenised asphaltene powder) the standard deviation (*s*) and the

relative standard deviation (RSD), or coefficient of variation (CV) are included as an estimate of data intermediate precision. Linearized probability plots are constructed with *Isoplot* (v 4.15). A normal distribution of the results is expected if sufficient data are obtained (Meisel and Moser 2004), in which case data points should be dispersed closely to a linear trend with a slope of 1 on a linearized probability plot (Ludwig 2012). In addition, histograms and probability density curves presented here also indicate the range and distribution pattern of the Re-Os data, although their shapes depend partially on the choice of bins and axis scale.

4.1 RM 8505 whole oil Re and Os and comparison with previous studies

The RM 8505 whole oil Re and Os mass fractions and isotope amount ratios are presented in Table 2 and Figure 1. The results of two whole oil analyses of RM 8505 by Georgiev *et al*. (2016) are also presented on the figures where appropriate for comparison.

The measurement results of eighteen RM 8505 whole oil test portions in this study range from 1.69 to 2.15 ng g^{-1} Re and 21.0 to 27.0 pg g^{-1} total Os (i.e. all Os isotopes), with the $^{187}Re/^{188}Os$ values ranging from 435 to 474 and $^{187}Os/^{188}Os$ compositions from 1.48 to 1.54. The mean values are 1.95 ± 0.06 ng g^{-1} for Re, 24.4 ± 0.8 pg g^{-1} for Os, 454 ± 5 for $^{187}Re/^{188}Os$ and 1.52 ± 0.01 for $^{187}Os/^{188}Os$ (n = 18, 95% conf.). These mean values are very similar to the median values, thus indicating a symmetrical distribution of the data. The linearized probability plots of the Re-Os data show that the Re-Os mass fraction and isotope amount ratio data points are distributed along linear trends with slopes of ~ 1 (0.95 ~ 1.02) indicating a similar to normal distribution of the data set. The histograms and the probability density curves of the isotope amount ratios are clearly similar to normal distributions, although this is less so for the Re and Os mass fractions. Besides the choice of the bins, the

250 less than normal distribution of the Re and Os mass fraction data is also due to the higher
251 precision of the isotope amount ratios compared to the Re and Os mass fractions, which is
252 also reflected by the lower RSD values for isotope amount ratio measurements.
253
254 The RM 8505 crude oil has also previously been analysed for Re-Os data by Sen and
255 Peucker-Ehrenbrink (2014) and Georgiev *et al*. (2016). Although slightly different methods
256 were applied, the results of these studies are consistent with the results of the present study.
257 These studies both applied HPA-S digestion instead of the Carius tube method. In addition,
258 Sen and Peucker-Ehrenbrink (2014) also sparged the OsO_4 of the digested solution directly
259 into MC-ICPMS for the measurement of $^{187}Os/^{188}Os$ values. The six measurements on 150 –
260 200 mg of RM 8505 by Sen and Peucker-Ehrenbrink (2014) yield Re and Os mass fractions
261 of 2.9 ± 1.5 ng g^{-1} and 28 ± 4 pg g^{-1}, respectively, with $^{187}Os/^{188}Os$ values of 1.62 ± 0.15 (1 *s*,
262 n = 6; Table 2). Although spreading over a relatively large range due to the incomplete
263 digestion as indicated by the authors, the results are broadly consistent with the results of the
264 present study. The measurement results of two test portions of RM 8505 (~ 300 mg) for Re
265 and Os mass fractions of Georgiev *et al*. (2016) are slightly higher than the present study
266 (2.28 and 2.30 vs 1.95 ± 0.25 ng g^{-1} Re; ~ 31.0 and 29.3 vs 24.4 ± 3.5 pg g^{-1} Os). However,
267 the $^{187}Os/^{188}Os$ compositions are indistinguishable (1.455 and 1.515 vs 1.52 ± 0.04), with
268 only one of the $^{187}Re/^{188}Os$ values being nominally lower than this study (419 and 443 vs 454
269 ± 20). Combining the results of Georgiev *et al*. (2016) with this study, the Re-Os
270 measurement on twenty test portions of RM 8505 gives mean values of 1.98 ± 0.07 ng g^{-1} of
271 Re, 25.0 ± 1.1 pg g^{-1} of Os, 452 ± 6 of $^{187}Re/^{188}Os$ and 1.51 ± 0.01 of $^{187}Os/^{188}Os$ (n = 20, 95%
272 conf.).

4.2 Rhenium and Os data of the individually separated asphaltene and maltene from RM 8505

The Re and Os mass fractions and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values of the individually separated asphaltene and maltene samples (eighteen of each type) from the RM 8505 whole oil are presented in Tables 3 and 4, and Figures 2 and 3, respectively. The asphaltene fraction possesses Re and total Os mass fractions from 13.47 to 14.56 ng g^{-1} and from 137.3 to 153.2 pg g^{-1}, respectively. The $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ measurement results of the asphaltene range from 543 to 570 and 1.57 to 1.65, respectively. The mean values are 14.04 ± 0.18 ng g^{-1} for Re, 145.4 ± 2.4 pg g^{-1} for total Os, 556 ± 4 for $^{187}Re/^{188}Os$ and 1.61 ± 0.01 for $^{187}Os/^{188}Os$ (n = 18, 95% conf.). The maltene fractions possess 0.22 to 0.27 ng g^{-1} Re and from 7.8 to 8.9 pg g^{-1} total Os, with $^{187}Re/^{188}Os$ values between 148 and 183 and $^{187}Os/^{188}Os$ compositions between 1.09 and 1.28. The mean values are 0.25 ± 0.01 ng g^{-1} for Re, 8.4 ± 0.2 pg g^{-1} for total Os, 161 ± 6 for $^{187}Re/^{188}Os$ and 1.20 ± 0.02 for $^{187}Os/^{188}Os$ (n = 18, 95% conf.). All of the Re-Os data means for the asphaltene and maltene fractions are similar to the corresponding median values.

The Re-Os data for the asphaltene and maltene fractions show linear trends on the linearized probability plots, with slopes of ~ 1 (0.97 ~ 1.02). The histograms and the probability density curves of the Re-Os mass fraction and isotope amount ratio data for the maltene fractions are very similar to normal distributions. Those of asphaltene isotope amount ratios are similar to normal distributions; however, more data are needed before this can be affirmed for asphaltene Re and Os mass fractions. The lower RSD values of the isotopic compositions indicate better data intermediate precision than for the Re and Os mass fractions for asphaltenes. The RSD values of maltenes are generally higher than those of the asphaltene

and whole oil samples. Overall the Re and Os mass fraction RSD values decrease from maltene to whole oil to asphaltene. This phenomenon indicates the increase in the data intermediate precision, which corresponds to the increased levels of Re and Os mass fractions, and the increase of sample to blank ratios.

4.3 The roles of asphaltene and maltene in the RM 8505 whole oil Re-Os systematics

4.3.1 Asphaltene and maltene separation of RM 8505

The asphaltene and maltene fractions of RM 8505 account for an average of ~ 13% and ~ 79% of the mass of crude oil (Table 6; Figure 6a). The mean loss of ~ 8% of sample during this separation process can largely be attributed to the loss of volatile light fractions and any water present during the drying of samples. For example, heating 0.3 g of RM 8505 crude oil at 80 °C for 10 days resulted in a mass loss of 4.4%. Further, additional minor sample loss can be accounted for during sample transfer, and additionally evaporation to remove the $CHCl_3$ used to transfer the sample.

4.3.2 Re and Os mass fractions and isotope amount ratio of asphaltene and maltene

The sums of the mass fractions of Re and Os for every pair of asphaltene and maltene separated from the same oil, weighted by their mass percentage, are from 1.86 to 2.11 ng g^{-1} Re and from 23.1 to 26.8 pg g^{-1} Os (Figure 6b-c; Table 6). These values are indistinguishable

from the Re and Os contents of whole oil (Table 2), indicating good mass balance and no significant Re or Os loss with the evaporated light fraction (Figure 6b-c). Disregarding any possible Re and Os in the volatile components, i.e. taking the aforementioned sums as the Re and Os mass fractions of the whole oil, the asphaltene fraction accounts for the majority of the whole oil Re (~ 90%) and Os (~ 74%), with the remaining Re (~ 10%) and Os (~ 26%) being bound in the maltene fraction (Table 6; Figure 6d-e). This observation is consistent with previous studies (Selby *et al.* 2007; Rooney *et al.* 2012; Lillis and Selby 2013; Cumming *et al.* 2014; Georgiev *et al.* 2016).

The $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ of the asphaltenes are closer to those of the RM 8505 crude oils when compared with the maltenes (Figure 5). It is typical that the Re-Os isotope systematics of whole oils are dominated by that of the asphaltene fractions as a direct result of the asphaltene fraction housing the majority of the Re and Os of a crude oil (Figures 6 - 7; Selby *et al.* 2007). For many of the oils studied by Selby *et al*. (2007), the asphaltene and whole oil of the same crude oil exhibit very similar (within uncertainty) $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$. However, in contrast, such isotope amount ratios of the maltene fraction can be similar, within uncertainty, to that of the whole oil and the asphaltene, but can also often differ significantly from that of the crude oil and asphaltene. The available data show that the maltene fractions can possess both lower $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ and/or lower $^{187}Re/^{188}Os$ and similar to higher $^{187}Os/^{188}Os$ to that of the whole oil and asphaltene fraction (Figure 7, this study; Selby *et al.* 2007; Georgiev *et al.* 2016). The explanation for the differences in the Re-Os isotope systematics of the maltene to that of the asphaltene and whole crude oil is currently not known.

The RM 8505 whole oil, asphaltene and maltene $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ define a line of best-fit that determines a Re-Os date of 62.7 ± 5.7 Ma (n = 54, initial $^{187}Os/^{188}Os$ = 1.030 ± 0.051, MSWD = 0.31). However, without detailed information with respect to the source of RM 8505 and accurate estimates of its generation age from the source, it is challenging to fully interpret the date given by the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ of the whole oil, asphaltene and maltene of RM 8505. This Re-Os date is older and only overlaps with the timing of the initial oil generation of the Venezuelan source rocks, i.e. Early Eocene, when the uncertainty is considered. As such, it is difficult to relate the Re-Os date to the known timing of any geological process associated with the Venezuelan petroleum systems, i.e., oil generation and the deposition of the source rock. In fact, we consider the outcome of the straight line of the Re-Os isotope data merely to be the illustration of the fractionation of RM 8505 crude oil Re and Os into the asphaltene and maltene fractions. However, any interpretation of the collective use of the Re-Os systematics of crude oil, asphaltene, and maltene from a single oil with respect to Re-Os geochronology of the petroleum system should be treated with caution before a more thorough knowledge of the Re and Os geochemistry of a crude oil is obtained.

4.4 Homogenised asphaltene

The Re-Os data of two different batches of the homogenised asphaltene (2×12, 2 samples from each bottle) are presented in Table 5 and Figure 8. The Re-Os measurement results for these asphaltene analyses range from 16.18 to 17.01 ng g^{-1} for Re and from 161.2 to 169.6 pg g^{-1} for total Os, with the $^{187}Re/^{188}Os$ values being between 558 and 592 and the $^{187}Os/^{188}Os$ compositions being between 1.61 and 1.67. The mean values of the Re-Os data, which are very similar to their medians, are 16.52 ± 0.10 ng g^{-1} for Re, 166.0 ± 0.9 pg g^{-1} for total Os, 574 ± 3 for $^{187}Re/^{188}Os$ and 1.64 ± 0.01 for $^{187}Os/^{188}Os$ (n = 24, 95% conf.). The linearized

probability plots, histograms and probability density curves illustrate the similar to normal distribution of the data. The different Re and Os mass fractions and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values of the homogenised asphaltene sample to the individually separated asphaltene samples is probably due to the lower asphaltene percentage of the whole oil (see below).

4.5 Comparing the suitability of whole oil, individually separated asphaltene and homogenised asphaltene as Re-Os measurement reference materials

Crude oil is a highly complex mixture of thousands of organic compounds and also water and minerals in many cases (Berridge *et al.* 1968). The intrinsic heterogeneity of liquid crude oil is a major problem for the intermediate precision of Re and Os mass fractions and isotope amount ratios (Heilmann *et al.* 2009; Ventura *et al.* 2015; e.g. Fe). This is reflected by the difference in Re-Os characteristics of whole oil samples in this study (Table 2). For example, there is heterogeneity among the RM 8505 bottles analysed in this study: bottle A contains less asphaltene and lower Re and Os mass fractions than the other bottles. In addition to the heterogeneity of the Re and Os bearing organic compounds in RM 8505, different water contents of the sampled oils could have also contributed to the variation of crude oil Re and Os elemental mass fractions. For the results of all the 20 measurements on the RM 8505 crude oil (Georgiev *et al.* 2016 and this study), the relative standard deviations in the Re and Os mass fractions are 7.8% and 9.5%, respectively. However, the relative standard deviations of the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ data are 2.8% and 1.6%, respectively, which are relatively low. Although the variance seems to be high for the Re and Os mass fractions, in general the results presented from the Re-Os measurements on the RM 8505 whole oil so far still fit for the purpose of serving as a petroleum matrix-matched reference material for Re-Os

measurements, especially considering the good data quality of the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ measurement results.

To avoid the influence of the heterogeneity of liquid oil, fine solid bitumen/asphaltene powder, which is easier to homogenise and keep homogenised can be used instead. The bitumen/asphaltene powder will still have typical petroleum sample Re and Os mass fractions, and keep the character of generating carbon dioxide during digestion of liquid crude oil samples. In fact, the ~ 90 g asphaltene in the form of homogenised fine solid powder yields the lowest Re-Os mass fractions and isotopic data RSD values of all sample types in this study. The precisions are also significantly reduced from the individually separated asphaltenes – each of which is from ~ 1 g of crude oil in this study and subject to the variation of asphaltene separation process (e.g. Table 6). This confirms the ability of solid asphaltene powder to reduce the influence of liquid crude oil Re-Os heterogeneity. The homogenised asphaltene can serve as a good reference material for both Re and Os mass fractions and isotope amount ratio determination.

5 Summary

The Re-Os elemental mass fraction and isotope amount ratio data of NIST RM 8505 whole oil and the homogenised asphaltene in this study, which were obtained via Carius Tube - Isotope Dilution - NTIMS methodology, entitle them as suitable matrix-matched reference material for petroleum Re-Os measurements. The Re-Os data and close to normal distribution and the RSD values are low. The establishment of these matrix-matched reference materials

should facilitate inter- and intra-laboratory comparison and method validation with regards to petroleum Re-Os measurements.

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References

Bandoniene, D., Zettl, D., Meisel, T., and Maneiko, M. (2013)
Suitability of elemental fingerprinting for assessing the geographic origin of pumpkin (Cucurbita pepo var. styriaca) seed oil: **Food Chemistry, v. 136, no. 3,** p. 1533-1542.

Berridge, S., Thew, M., and Loriston-Clarke, A. (1968)
The formation and stability of emulsions of water in crude petroleum and similar stocks: **Journal of the Institute of Petroleum, v. 54, no. 539,** p. 333-357.

Birck, J. L., Barman, M. R., and Capmas, F. (1997)
Re-Os Isotopic Measurements at the Femtomole Level in Natural Samples: **Geostandards and Geoanalytical Research, v. 21, no. 1,** p. 19-27.

Cohen, A. S., Coe, A. L., Bartlett, J. M., and Hawkesworth, C. J. (1999)
Precise Re–Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater: **Earth and Planetary Science Letters, v. 167, no. 3-4,** p. 159-173.

Cohen, A. S., and Waters, F. G. (1996)
Separation of osmium from geological materials by solvent extraction for analysis by thermal ionisation mass spectrometry: **Analytica Chimica Acta, v. 332, no. 2,** p. 269-275.

Creaser, R. A., Papanastassiou, D. A., and Wasserburg, G. J. (1991)
Negative thermal ion mass spectrometry of osmium, rhenium and iridium: **Geochimica et Cosmochimica Acta, v. 55, no. 1,** p. 397-401.

Cumming, G. L. (1969)
A recalculation of the age of the solar system: **Canadian Journal of Earth Sciences, v. 6, no. 4**, p. 719-735

Cumming, V. M., Selby, D., and Lillis, P. G. (2012)
Re–Os geochronology of the lacustrine Green River Formation: Insights into direct depositional dating of lacustrine successions, Re–Os systematics and paleocontinental weathering: **Earth and Planetary Science Letters, v. 359-360,** p. 194-205.

Cumming, V. M., Selby, D., Lillis, P. G., and Lewan, M. D. (2014)
Re–Os geochronology and Os isotope fingerprinting of petroleum sourced from a Type I lacustrine kerogen: Insights from the natural Green River petroleum system in the Uinta Basin and hydrous pyrolysis experiments: **Geochimica et Cosmochimica Acta, v. 138,** p. 32-56.

Finlay, A. J., Selby, D., and Osborne, M. J. (2011)
Re-Os geochronology and fingerprinting of United Kingdom Atlantic margin oil: Temporal implications for regional petroleum systems: **Geology, v. 39, no. 5,** p. 475-478.

Finlay, A. J., Selby, D., and Osborne, M. J. (2012)
Petroleum source rock identification of United Kingdom Atlantic Margin oil fields and the Western Canadian Oil Sands using Platinum, Palladium, Osmium and Rhenium: Implications for global petroleum systems: **Earth and Planetary Science Letters, v. 313-314,** p. 95-104.

Finlay, A. J., Selby, D., Osborne, M. J., and Finucane, D. (2010)
Fault-charged mantle-fluid contamination of United Kingdom North Sea oils: Insights from Re-Os isotopes: **Geology, v. 38, no. 11,** p. 979-982.

Ge, X., Shen, C., Selby, D., Deng, D., and Mei, L. (2016)
Apatite fission-track and Re-Os geochronology of the Xuefeng uplift, China: Temporal implications for dry gas associated hydrocarbon systems: **Geology, v. 44, no. 6,** p. 491-494.

Georgiev, S. V., Stein, H. J., Hannah, J. L., Galimberti, R., Nali, M., Yang, G., and Zimmerman, A. (2016)
Re-Os dating of maltenes and asphaltenes within single samples of crude oil: **Geochimica Et Cosmochimica Acta, v. 179,** p. 53-75.

Gramlich, J. W., Murphy, T. J., Garner, E. L., and Shields, W. R. (1973)
Absolute isotopic abundance ratio and atomic weight of a reference sample of rhenium: **J. Res. Natl. Bur. Stand. A, v. 77,** p. 691-698.

Heilmann, J., Boulyga, S. F., and Heumann, K. G. (2009)
Development of an isotope dilution laser ablation ICP-MS method for multi-element determination in crude and fuel oil samples: **Journal of Analytical Atomic Spectrometry, v. 24, no. 4,** p. 385-390.

James, K. (1990)
The Venezuelan hydrocarbon habitat: **Geological Society, London, Special Publications, v. 50, no. 1,** p. 9-35.

James, K. (2000)
The Venezuelan hydrocarbon habitat, part 1: tectonics, structure, palaeogeography and source rocks: **Journal of Petroleum Geology, v. 23, no. 1,** p. 5-53.

Li, C., Qu, W.-J., Wang, D.-H., Chen, Z.-H., Du, A.-D., and Zhang, C.-Q. (2011)
Dissolving Experimental Research of Re-Os Isotope System for Bitumen Samples: **Rock and Mineral Analysis, v. 30, no. 6,** p. 688-694.

Lillis, P. G., and Selby, D. (2013)
Evaluation of the rhenium–osmium geochronometer in the Phosphoria petroleum system, Bighorn Basin of Wyoming and Montana, USA: **Geochimica et Cosmochimica Acta, v. 118,** p. 312-330.

Ludwig, K. R. (1980)
Calculation of uncertainties of U-Pb isotope data: **Earth and Planetary Science Letters, v. 46, no. 2**, p. 212-220

Ludwig, K. (2012)
User's manual for Isoplot version 3.75-4.15: a geochronological toolkit for Microsoft: **Excel Berkley Geochronological Center Special Publication, no. 5,** 76 p.

Luguet, A., Nowell, G. M., and Pearson, D. G. (2008)
$^{184}Os/^{188}Os$ and $^{186}Os/^{188}Os$ measurements by Negative Thermal Ionisation Mass Spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision: **Chemical Geology, v. 248, no. 3**, p. 342-362.

Mahdaoui, F., Michels, R., Reisberg, L., Pujol, M., and Poirier, Y. (2015)
Behavior of Re and Os during contact between an aqueous solution and oil: Consequences for the application of the Re–Os geochronometer to petroleum: **Geochimica et Cosmochimica Acta, v. 158,** p. 1-21.

Mahdaoui, F., Reisberg, L., Michels, R., Hautevelle, Y., Poirier, Y., and Girard, J.-P. (2013)
Effect of the progressive precipitation of petroleum asphaltenes on the Re–Os radioisotope system: **Chemical Geology, v. 358,** p. 90-100.

Marques, J. C. (2013)
Overview on the Re-Os isotopic method and its application on ore deposits and organic-rich rocks: **Geochimica Brasiliensis, v. 26, no. 1,** p. 49-66.

Meisel, T., and Moser, J. (2004)
Reference materials for geochemical PGE analysis: new analytical data for Ru, Rh, Pd, Os, Ir, Pt and Re by isotope dilution ICP-MS in 11 geological reference materials: **Chemical Geology, v. 208, no. 1-4,** p. 319-338.

Meisel, T., Reisberg, L., Moser, J., Carignan, J., Melcher, F., and Brügmann, G. (2003)
Re–Os systematics of UB-N, a serpentinized peridotite reference material: **Chemical Geology, v. 201, no. 1,** p. 161-179.

Morgan, J., Golightly, D., and Dorrzapf, A. (1991)
Methods for the separation of rhenium, osmium and molybdenum applicable to isotope geochemistry: **Talanta, v. 38, no. 3,** p. 259-265.

Nier, A. O. (1937)

The isotopic constitution of osmium: **Physical Review, v. 52, no. 8,** p. 885.

Nowell, G., Luguet, A., Pearson, D., and Horstwood, M. (2008)
Precise and accurate $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ measurements by multi-collector plasma ionisation mass spectrometry (MC-ICP-MS) part I: Solution analyses: **Chemical Geology, v. 248, no. 3,** p. 363-393.

Qi, L., Gao, J.-F., Zhou, M.-F., and Hu, J. (2013)
The Design of Re-usable Carius Tubes for the Determination of Rhenium, Osmium and Platinum-Group Elements in Geological Samples: **Geostandards and Geoanalytical Research, v. 37, no. 3,** p. 345-351.

Reisberg, L., and Meisel, T. (2002)
The Re-Os Isotopic System: A Review of Analytical Techniques: **Geostandards Newsletter, v. 26, no. 3,** p. 249-267.

Rooney, A. D., Selby, D., Lewan, M. D., Lillis, P. G., and Houzay, J.-P. (2012)
Evaluating Re–Os systematics in organic-rich sedimentary rocks in response to petroleum generation using hydrous pyrolysis experiments: **Geochimica et Cosmochimica Acta, v. 77,** p. 275-291.

Schmitz, M.D. and Schoene, B. (2007)
Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using ^{205}Pb-^{135}U-(^{233}U)-spiked isotope dilution thermal ionization mass spectrometric data: **Geochemistry, Geophysics, Geosystems, v. 8, no. 8**, 20 p.

Selby, D., Creaser, R., Dewing, K., and Fowler, M. (2005)
Evaluation of bitumen as a Re–Os geochronometer for hydrocarbon maturation and migration: A test case from the Polaris MVT deposit, Canada: **Earth and Planetary Science Letters, v. 235, no. 1-2,** p. 1-15.

Selby, D., and Creaser, R. A. (2001)
Re-Os geochronology and systematics in molybdenite from the Endako porphyry molybdenum deposit, British Columbia, Canada: **Economic Geology, v. 96, no. 1,** p. 197-204.

Selby, D., and Creaser, R. A. (2005)
Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes: **Science, v. 308, no. 5726,** p. 1293-1295.

Selby, D., Creaser, R. A., and Fowler, M. G. (2007)
Re–Os elemental and isotopic systematics in crude oils: **Geochimica et Cosmochimica Acta, v. 71, no. 2,** p. 378-386.

Sen, I. S., and Peucker-Ehrenbrink, B. (2014)
Determination of Osmium Concentrations and $^{187}Os/^{188}Os$ of Crude Oils and Source Rocks by Coupling High-Pressure, High-Temperature Digestion with Sparging OsO4 into a Multicollector Inductively Coupled Plasma Mass Spectrometer: **Analytical chemistry, v. 86, no. 6,** p. 2982-2988.

Shirey, S. B., and Walker, R. J. (1995)
Carius tube digestion for low-blank rhenium-osmium analysis: **Analytical Chemistry, v. 67, no. 13,** p. 2136-2141.

Speight, J. (2004)
Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum: **Oil & gas science and technology, v. 59, no. 5,** p. 467-477.

Steven, N., Creaser, R., Wulff, K., Kisters, A., Eglington, B., and Miller, J. (2015)
Implications of high-precision Re-Os molybdenite dating of the Navachab orogenic gold deposit, Namibia: Geochemistry: **Exploration, Environment, Analysis, v. 15, no. 2-3,** p. 125-130.

Summa, L., Goodman, E., Richardson, M., Norton, I., and Green, A. (2003)
Hydrocarbon systems of Northeastern Venezuela: plate through molecular scale-analysis of the genesis and evolution of the Eastern Venezuela Basin: **Marine and Petroleum Geology, v. 20, no. 3,** p. 323-349.

Ventura, G. T., Gall, L., Siebert, C., Prytulak, J., Szatmari, P., Hürlimann, M., and Halliday, A. N. (2015)
The stable isotope composition of vanadium, nickel, and molybdenum in crude oils: **Applied Geochemistry, v. 59,** p. 104-117.

Völkening, J., T. Walczyk, and K.G. Heumann (1991)
Osmium isotope ratio determination by negative thermal ion mass spectrometry: International **Journal of Mass Spectrometry and Ion Processes, v. 105, no. 2,** p. 147–159.

Walczyk, T. (2004)
TIMS versus multicollector-ICP-MS: coexistence or struggle for survival?: **Analytical and bioanalytical chemistry, v. 378, no. 2,** p. 229-231.

Zimmerman, A., Stein, H. J., Morgan, J. W., Markey, R. J., and Watanabe, Y. (2014)
Re–Os geochronology of the El Salvador porphyry Cu–Mo deposit, Chile: Tracking analytical improvements in accuracy and precision over the past decade: **Geochimica et Cosmochimica Acta, v. 131,** p. 13-32.

Figures and tables

Table 1 Total procedural blanks of rhenium and osmium, and $^{187}Os/^{188}Os$ composition during the study.

Blank ID	Re (pg)	u	Os (fg)	u	$^{187}Re/^{188}Os$	u	$^{187}Os/^{188}Os$	u	rho
RO539-13	1.61	0.03	64.6	0.4	121	2	0.227	0.005	0.28
RO549-4	1.63	0.03	98.8	0.7	81	2	0.302	0.009	0.21
RO560-19	1.53	0.02	39.0	0.7	217	8	1.255	0.063	0.55
RO560-21	9.76	0.16	95.3	14.1	527	183	0.643	0.363	0.61
RO631-7	5.82	0.09	89.4	0.5	318	6	0.230	0.004	0.29
RO713-7	3.70	0.06	52.5	4.4	356	71	0.495	0.141	0.69
RO728-6	2.16	0.03	46.4	5.8	225	63	0.168	0.242	0.19

u: expanded (k = 2) combined standard uncertainties which include the uncertainties in weighing, blank correction and spike calibrations, mass spectrometry measurements of Re and Os, and the intermediate precision of the results of repeated measurements of Re and Os reference solution.
Os: all Os isotopes
rho: error correlation value between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$

653 Table 2 Rhenium and osmium mass fractions and isotope amount ratios of RM 8505 whole oil.

Sample	Re ($ng\ g^{-1}$)	u	Total Os ($pg\ g^{-1}$)	u	^{192}Os ($pg\ g^{-1}$)	u	$^{187}Re/^{188}Os$	u	$^{187}Os/^{188}Os$	u	rho
A	1.86	0.04	22.5	0.9	7.8	0.7	474	43	1.54	0.18	0.72
A	1.69	0.04	21.0	0.9	7.3	0.7	459	42	1.53	0.18	0.72
A	1.88	0.04	23.4	0.9	8.2	0.7	458	41	1.53	0.18	0.72
A	1.84	0.04	22.9	0.9	8.0	0.7	456	41	1.53	0.18	0.72
A	1.94	0.04	24.3	1.0	8.5	0.7	455	41	1.52	0.18	0.72
A	1.77	0.04	22.2	0.9	7.8	0.7	454	42	1.53	0.18	0.72
mean of A:	1.83		22.7		7.9		459		1.53		
1 *s*	0.09		1.1		0.4		7		0.01		
B	2.15	0.04	27.0	1.1	9.4	0.8	454	40	1.51	0.18	0.71
B	2.06	0.04	26.0	1.0	9.1	0.8	450	40	1.49	0.18	0.71
B	2.09	0.04	26.8	1.1	9.4	0.8	442	39	1.48	0.17	0.71
mean of B:	2.10		26.6		9.3		449		1.49		
1 *s*	0.05		0.6		0.2		6		0.02		
C	1.94	0.04	25.0	1.0	8.8	0.8	441	40	1.51	0.18	0.71
C	1.88	0.04	23.6	0.9	8.3	0.7	453	41	1.52	0.18	0.72
C	1.88	0.04	23.6	0.9	8.2	0.7	454	41	1.54	0.18	0.72
mean of C:	1.90		24.1		8.4		449		1.52		
1 *s*	0.04		0.8		0.3		7		0.02		
D	1.94	0.04	24.4	1.0	8.5	0.7	454	41	1.53	0.18	0.72
D	2.03	0.04	26.3	1.0	9.2	0.8	439	39	1.49	0.18	0.71
D	1.97	0.04	25.7	1.0	9.0	0.8	435	39	1.49	0.18	0.71
mean of D:	1.98		25.5		8.9		443		1.50		
1 *s*	0.05		1.0		0.4		10		0.02		

E	2.05	0.04	25.4	1.0	8.9	0.8	460	41	1.53	0.18	0.72
E	2.01	0.04	24.8	1.0	8.7	0.8	461	41	1.53	0.18	0.72
E	2.06	0.04	24.8	1.0	8.7	0.8	472	42	1.49	0.18	0.72
mean of E:	2.04		25.0		8.7		464		1.52		
1 *s*	0.03		0.3		0.1		6		0.02		
median of all	1.94		24.6		8.6		454		1.52		
mean of all	1.95		24.4		8.5		454		1.52		
1 *s* of all	0.12		1.7		0.6		10		0.02		
RSD of all	6.2%		6.8%		6.9%		2.2%		1.3%		
CI	0.06		0.8		0.3		5		0.01		
Georgiev *et al*. (2016)											
SVG-1	2.30	0.03	31.0	0.1	np	np	419.0	6.9	1.455	0.007	0.170
SVG-2	2.28	0.03	29.3	0.1	np	np	442.9	7.8	1.515	0.008	0.149
combining the data of this study and Georgiev *et al*. (2016):											
median	1.96		24.8		8.6		454		1.52		
mean	1.98		25.0		8.5		452		1.51		
1 *s*	0.15		2.4		0.6		12		0.02		
RSD	7.8%		9.5%		6.9%		2.8%		1.6%		
CI	0.07		1.1		0.3		6		0.01		
Sen and Peucker-Ehrenbrink (2014)											
8505_1	5.1	np	21.7	0.4	np	np	np	np		0.03	
8505_2	1.9	np	28.9	0.5	np	np	np	np	1.69	0.04	
8505_2 repeat	np	np	27.9	0.7	np	np	np	np	1.74	0.07	
8505_3	1.9	np	27.4	0.4	np	np	np	np	1.53	0.04	
8505_4	2.7	np	35.6	0.5	np	np	np	np	1.67	0.03	

8505_5	np	np	28.8	0.5	np	np	np	np	1.55	0.02
8505_6	np	np	27.0	0.4	np	np	np	np	1.36	0.02
mean	2.9		28						1.62	
1 *s*	1.5		4						0.15	

u: expanded (k = 2) combined standard uncertainties, see footnote of Table 1 for details
Total Os: all Os isotopes
rho: error correlation value between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$
1 *s*: 1 standard deviation
RSD: relative standard deviation, also known as coefficient of variation
CI: 95% confidence interval under Student-t distribution
np: data not present in publication

665 Table 3 Rhenium and osmium mass fractions and isotope amount ratios of the individually separated asphaltene from RM 8505.

666

Sample	Re (ng g^{-1})	u	Total Os (pg g^{-1})	u	^{192}Os (pg g^{-1})	u	^{187}Re/^{188}Os	u	^{187}Os/^{188}Os	u	rho
A 1	13.68	0.07	140.3	1.8	48.4	1.0	562	12	1.63	0.05	0.71
A 2	13.54	0.07	138.6	1.8	47.8	1.0	563	12	1.64	0.05	0.71
A 3	13.47	0.06	137.3	1.8	47.4	1.0	566	12	1.64	0.05	0.71
A 4	13.61	0.07	138.8	1.8	47.8	1.0	566	12	1.64	0.05	0.71
A 5	13.71	0.07	139.7	1.8	48.2	1.0	566	12	1.64	0.05	0.71
A 6	14.56	0.06	147.5	1.9	50.8	1.1	570	12	1.65	0.05	0.71
mean of A:	13.76		140.4		48.4		565		1.64		
1 *s*	0.40		3.6		1.2		3		0.01		
B 1	14.50	0.06	153.2	2.0	53.0	1.1	544	12	1.60	0.05	0.70
B 2	13.73	0.06	143.4	1.9	49.7	1.0	550	12	1.60	0.05	0.71
B 3	13.96	0.06	145.2	1.9	50.2	1.1	553	12	1.62	0.05	0.71
mean of B:	14.06		147.3		51.0		549		1.60		
1 *s*	0.40		5.2		1.8		5		0.01		
C 1	14.19	0.06	147.8	1.9	51.2	1.1	551	12	1.60	0.05	0.71
C 2	14.28	0.06	148.4	1.9	51.5	1.1	551	12	1.57	0.05	0.71
C 3	14.00	0.06	148.2	1.9	51.3	1.1	543	12	1.61	0.05	0.71
mean of C:	14.15		148.2		51.3		548		1.59		
1 *s*	0.14		0.3		0.2		5		0.02		
D 1	14.17	0.06	149.1	1.9	51.6	1.1	546	12	1.60	0.05	0.71
D 2	14.55	0.07	152.6	2.0	52.9	1.1	547	12	1.59	0.05	0.71
D 3	13.77	0.06	143.7	1.9	49.7	1.0	551	12	1.60	0.05	0.71
mean of D:	14.16		148.4		51.4		548		1.60		

1 *s*	0.39		4.5		1.6		2		0.01		
E 1	14.26	0.06	148.1	1.9	51.4	1.1	553	12	1.59	0.05	0.70
E 2	14.31	0.07	148.1	1.9	51.3	1.1	555	12	1.60	0.05	0.71
E 3	14.50	0.07	147.5	1.9	51.1	1.1	565	12	1.60	0.05	0.71
mean of E:	14.36		147.9		51.3		557		1.59		
1 *s*	0.13		0.3		0.1		6		0.01		
median of all	14.08		147.5		50.9		553		1.60		
mean of all	14.04		145.4		50.3		556		1.61		
1 *s* of all	0.37		4.8		1.7		9		0.02		
RSD of all	2.6%		3.3%		3.5%		1.6%		1.3%		
CI	0.18		2.4		0.9		4		0.01		

u: expanded (k = 2) combined standard uncertainties, see footnote of Table 1 for details
Total Os: all Os isotopes
rho: error correlation value between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$
1 *s*: 1 standard deviation
RSD: relative standard deviation, also known as coefficient of variation
CI: 95% confidence interval under Student-t distribution

677 Table 4 Rhenium and osmium mass fractions and isotope amount ratios of the individually separated maltene from RM 8505.

678

Sample	Re ($ng\ g^{-1}$)	u	Total Os ($pg\ g^{-1}$)	u	^{192}Os ($pg\ g^{-1}$)	u	$^{187}Re/^{188}Os$	u	$^{187}Os/^{188}Os$	u	rho
A 1	0.25	0.04	8.1	0.4	2.9	0.3	173	34	1.25	0.19	0.52
A 2	0.26	0.04	8.7	0.4	3.1	0.3	163	32	1.21	0.18	0.50
A 3	0.25	0.04	7.8	0.4	2.8	0.3	179	36	1.22	0.19	0.53
A 4	0.27	0.04	8.7	0.4	3.1	0.3	172	32	1.22	0.18	0.52
A 5	0.27	0.04	8.1	0.4	2.9	0.3	183	35	1.28	0.19	0.54
A 6	0.27	0.04	8.2	0.4	3.0	0.3	183	35	1.24	0.18	0.54
mean of A:	0.26		8.3		3.0		176		1.24		
1 *s*	0.01		0.4		0.1		8		0.03		
B 1	0.23	0.04	8.2	0.4	3.0	0.4	155	36	1.22	0.19	0.48
B 2	0.23	0.04	8.1	0.4	2.9	0.4	153	33	1.18	0.18	0.48
B 3	0.23	0.04	8.4	0.4	3.1	0.4	148	31	1.13	0.17	0.47
mean of B:	0.23		8.2		3.0		152		1.18		
1 *s*	0.00		0.2		0.1		4		0.04		
C 1	0.24	0.04	8.7	0.4	3.1	0.4	154	31	1.19	0.17	0.48
C 2	0.23	0.04	8.6	0.4	3.1	0.4	150	31	1.20	0.18	0.48
C 3	0.24	0.04	8.7	0.4	3.2	0.4	148	29	1.16	0.17	0.48
mean of C:	0.24		8.6		3.1		150		1.18		
1 *s*	0.01		0.1		0.0		3		0.02		
D 1	0.22	0.04	8.2	0.4	3.0	0.3	149	32	1.09	0.16	0.47
D 2	0.25	0.04	8.7	0.5	3.1	0.4	158	33	1.22	0.18	0.49
D 3	0.24	0.04	8.5	0.4	3.1	0.4	152	31	1.18	0.17	0.48
mean of D:	0.24		8.5		3.1		153		1.16		

1 *s*	0.01		0.3		0.1		5		0.07		
E 1	0.24	0.04	8.0	0.4	2.9	0.4	162	33	1.22	0.18	0.50
E 2	0.24	0.04	8.9	0.4	3.2	0.4	148	30	1.20	0.17	0.48
E 3	0.27	0.04	8.8	0.4	3.2	0.3	167	31	1.18	0.17	0.51
mean of E:	0.25		8.6		3.1		159		1.20		
1 *s*	0.02		0.5		0.2		10		0.02		
median of all	0.24		8.5		3.1		157		1.21		
mean of all	0.25		8.4		3.0		161		1.20		
1 *s* of all	0.02		0.3		0.1		12		0.04		
RSD of all	6.7%		3.9%		4.0%		7.7%		3.7%		
CI	0.01		0.2		0.1		6		0.02		

u: expanded (k = 2) combined standard uncertainties, see footnote of Table 1 for details
Total Os: all Os isotopes
rho: error correlation value between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$
1 *s*: 1 standard deviation
RSD: relative standard deviation, also known as coefficient of variation
CI: 95% confidence interval under Student-t distribution

689 Table 5 Rhenium and osmium mass fractions and isotope amount ratios of the homogenised asphaltene.

690

Sample	Re (ng g^{-1})	u	Total Os (pg g^{-1})	u	^{192}Os (pg g^{-1})	u	^{187}Re/^{188}Os	u	^{187}Os/^{188}Os	u	rho
A1	16.73	0.06	166.9	1.6	57.6	0.7	578	8	1.64	0.03	0.71
A1'	16.67	0.06	167.3	1.5	57.5	0.7	576	7	1.67	0.03	0.71
A2	16.88	0.06	167.3	1.6	57.7	0.7	582	8	1.64	0.03	0.71
A2'	16.33	0.06	165.2	1.4	56.9	0.7	571	7	1.65	0.03	0.71
A3	16.33	0.06	161.2	1.5	55.5	0.7	585	8	1.65	0.03	0.71
A3'	16.18	0.06	162.6	1.4	56.1	0.7	574	7	1.64	0.03	0.71
A4	16.28	0.06	162.8	1.5	56.1	0.7	577	8	1.64	0.03	0.71
A4'	16.46	0.08	168.0	1.5	57.9	0.8	566	8	1.65	0.03	0.72
A5	16.30	0.06	165.0	1.5	56.8	0.7	570	8	1.65	0.03	0.71
A5'	16.45	0.06	166.6	1.5	57.4	0.7	570	7	1.65	0.03	0.71
A6	16.72	0.06	166.9	1.6	57.7	0.7	577	8	1.61	0.03	0.71
A6'	16.40	0.06	165.6	1.4	57.1	0.7	572	7	1.64	0.03	0.71
A7	16.32	0.06	167.6	1.6	57.9	0.7	561	7	1.62	0.03	0.71
A7'	17.00	0.06	165.8	1.4	57.2	0.7	592	7	1.64	0.03	0.71
A8	16.75	0.06	166.1	1.6	57.2	0.7	582	8	1.65	0.03	0.71
A8'	16.50	0.06	169.0	1.5	58.3	0.7	563	7	1.63	0.03	0.71
A9	16.52	0.06	167.1	1.6	57.6	0.7	571	8	1.65	0.03	0.71
A9'	17.01	0.06	169.6	1.5	58.5	0.7	578	7	1.64	0.03	0.71
A10	16.37	0.06	165.9	1.6	57.2	0.7	569	8	1.64	0.03	0.71
A10'	16.52	0.06	166.0	1.4	57.2	0.7	575	7	1.65	0.03	0.71
A11	16.40	0.06	164.9	1.5	56.9	0.7	574	8	1.64	0.03	0.71
A11'	16.67	0.06	163.7	1.4	56.4	0.7	588	7	1.65	0.03	0.71
A12	16.32	0.06	163.8	1.5	56.5	0.7	574	8	1.63	0.03	0.71
A12'	16.44	0.06	169.5	1.5	58.7	0.7	558	7	1.61	0.03	0.70
median	16.46		166.1		57.2		574		1.64		

mean	16.52	166.0	57.2	574	1.64
1 s	0.23	2.1	0.8	8	0.01
RSD	1.4%	1.3%	1.3%	1.4%	0.7%
CI	0.10	0.9	0.3	3	0.01

u: expanded (k = 2) combined standard uncertainties, see footnote of Table 1 for details
Total Os: all Os isotopes
rho: error correlation value between $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$
1 s: 1 standard deviation
RSD: relative standard deviation, also known as coefficient of variation
CI: 95% confidence interval under Student-t distribution

701 Table 6 Asphaltene and maltene mass percentage and the proportions of their total Re and Os contents, i.e. those of the whole oil of RM 8505

702 (regardless of the lost fractions)

703

	fractions (%)			Total of asphaltene and maltene			asphaltene percentage (%)		maltene percentage (%)	
sample	asphaltene	maltene	loss	Re (ng g^{-1})	Os (pg g^{-1})	^{187}Os (pg g^{-1})	Re	Os	Re	Os
A 1	12.2	79.8	8.0	1.87	23.5	4.0	89.2	72.6	10.8	27.4
A 2	12.5	77.6	9.9	1.89	24.1	4.0	89.5	72.0	10.5	28.0
A 3	12.3	79.3	8.4	1.86	23.1	3.9	89.2	73.3	10.8	26.7
A 4	12.1	79.6	8.2	1.87	23.8	4.0	88.4	70.9	11.6	29.1
A 5	12.1	80.0	7.9	1.88	23.4	4.0	88.5	72.2	11.5	27.8
A 6	11.2	82.3	6.5	1.86	23.3	3.9	87.9	70.9	12.1	29.1
	the range of A whole oil values (Table 2):			1.69 - 1.94	21.0 - 24.3	3.5 - 4.1				
B 1	13.3	78.4	8.3	2.11	26.8	4.5	91.4	76.1	8.6	23.9
B 2	13.4	79.2	7.4	2.02	25.6	4.2	91.1	75.0	8.9	25.0
B 3	12.9	83.8	3.3	1.99	25.8	4.2	90.4	72.6	9.6	27.4
	the range of B whole oil values (Table 2):			2.06 - 2.15	26.0 - 27.0	4.3 - 4.5				
C 1	13.5	78.8	7.7	2.10	26.7	4.4	90.9	74.4	9.1	25.6
C 2	13.1	77.7	9.3	2.05	26.0	4.3	91.2	74.5	8.8	25.5
C 3	13.3	77.7	9.0	2.04	26.4	4.4	91.0	74.4	9.0	25.6
	the range of C whole oil values (Table 2):			1.88 - 1.94	23.6 - 25.0	4.0 - 4.2				
D 1	13.3	76.6	10.1	2.06	26.1	4.3	91.7	76.1	8.3	23.9
D 2	13.0	78.6	8.4	2.09	26.7	4.4	90.6	74.3	9.4	25.7
D 3	13.4	79.2	7.4	2.03	25.9	4.3	90.8	74.0	9.2	26.0
	the range of D whole oil values (Table 2):			1.94 - 2.03	24.4 - 26.3	4.1 - 4.3				

E 1	12.9	81.1	6.0	2.03	25.6	4.2	90.6	74.6	9.4	25.4
E 2	13.2	79.4	7.4	2.07	26.5	4.4	90.8	73.4	9.2	26.6
E 3	13.0	77.9	9.1	2.09	26.0	4.3	90.0	73.6	10.0	26.4
the range of E whole oil values (Table 2):				2.01 - 2.06	24.8 - 25.4	4.1 - 4.3				
the range of all whole oil values (Table 2):				1.69 - 2.15	21.0 - 27.0	3.5 - 4.5				
median	13.0	79.2	8.1	2.03	25.8	4.2	90.6	73.8	9.4	26.2
mean	12.8	79.3	7.9	1.99	25.3	4.2	90.2	73.6	9.8	26.4
1 *s*	0.006	0.017	0.016	0.09	1.3	0.2	0.011	0.015	0.011	0.015
RSD	4.7%	2.2%	19.7%	4.8%	5.3%	4.5%	1.2%	2.1%	11.5%	5.8%
CI	0.3%	0.9%	0.8%	0.05	0.7	0.1	0.6%	0.8%	0.6%	0.8%

1 *s*: 1 standard deviation
RSD: relative standard deviation, also known as coefficient of variation
CI: 95% confidence interval under Student-t distribution

Figure 1 Linearized probability plots (top) and histograms and probability density curves (bottom) of RM 8505 whole oil Re-Os data. The Os data represents the total Os mass fraction. The linearized probability data points are plotted with the 1 *s* level combined measurement uncertainties of the measurement process. Two whole oil sample Re-Os results from Georgiev *et al.* (2016) are also plotted (in the dashed boxes) except the Os data as the values exceed the range of the plot (see Table 2).

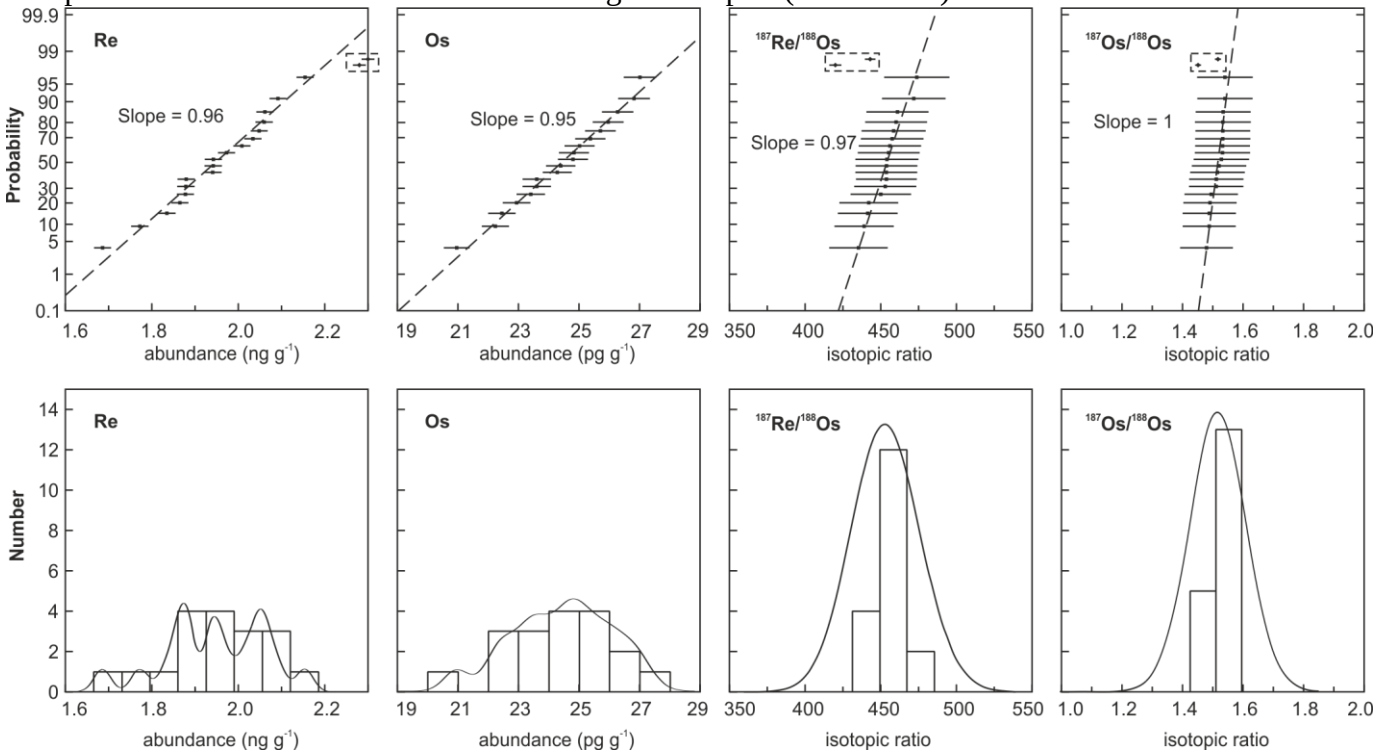


Figure 2 Linearized probability plots (top) and histograms and probability density curves (bottom) for individually separated asphaltene Re-Os data. The Os data represents the total Os mass fraction (i.e. all Os isotopes). The linearized probability data points are plotted with the 1 *s* level combined measurement uncertainties of the measurement process (see Table 3).

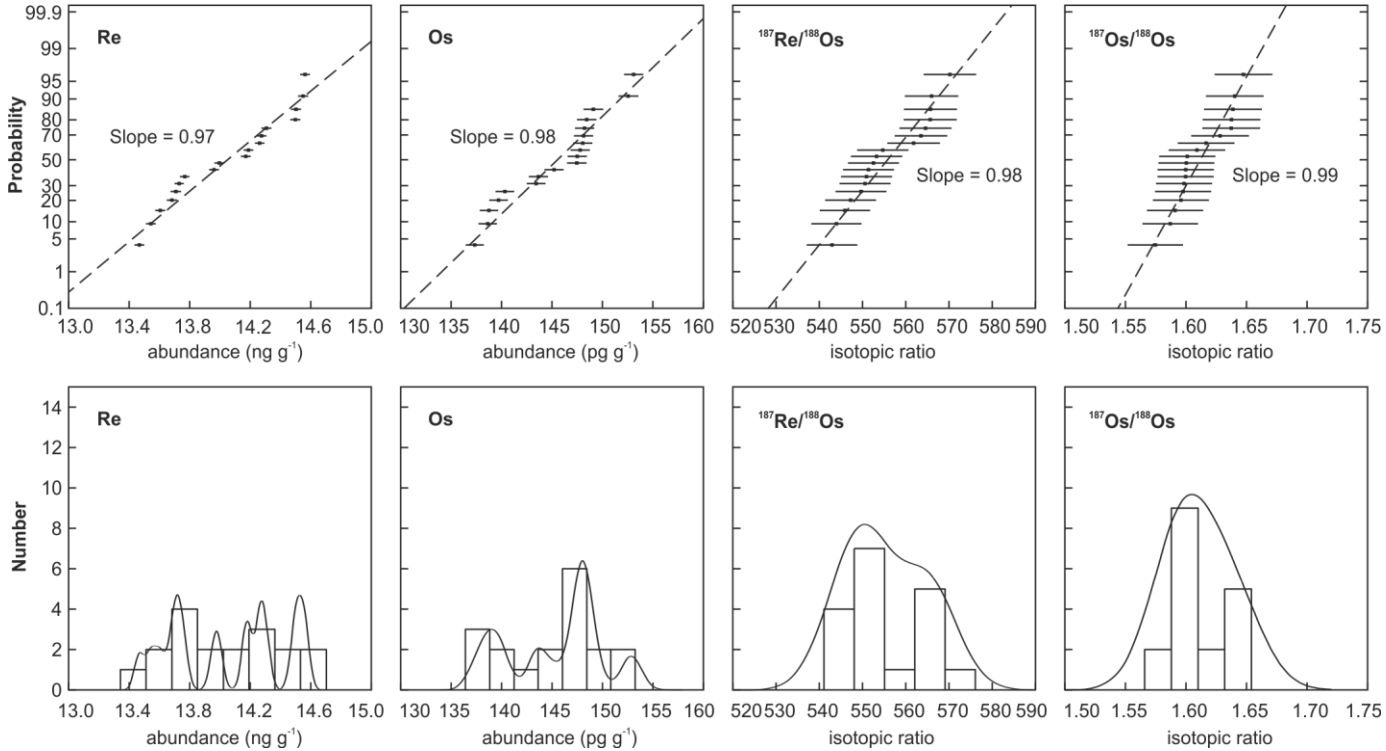


Figure 3 Linearized probability plots (top) and histograms and probability density curves (bottom) of separated maltene Re-Os data. Os data are for total Os. The linearized probability data points are plotted with the 1 *s* level combined measurement uncertainties of the measurement process(see Table 4).

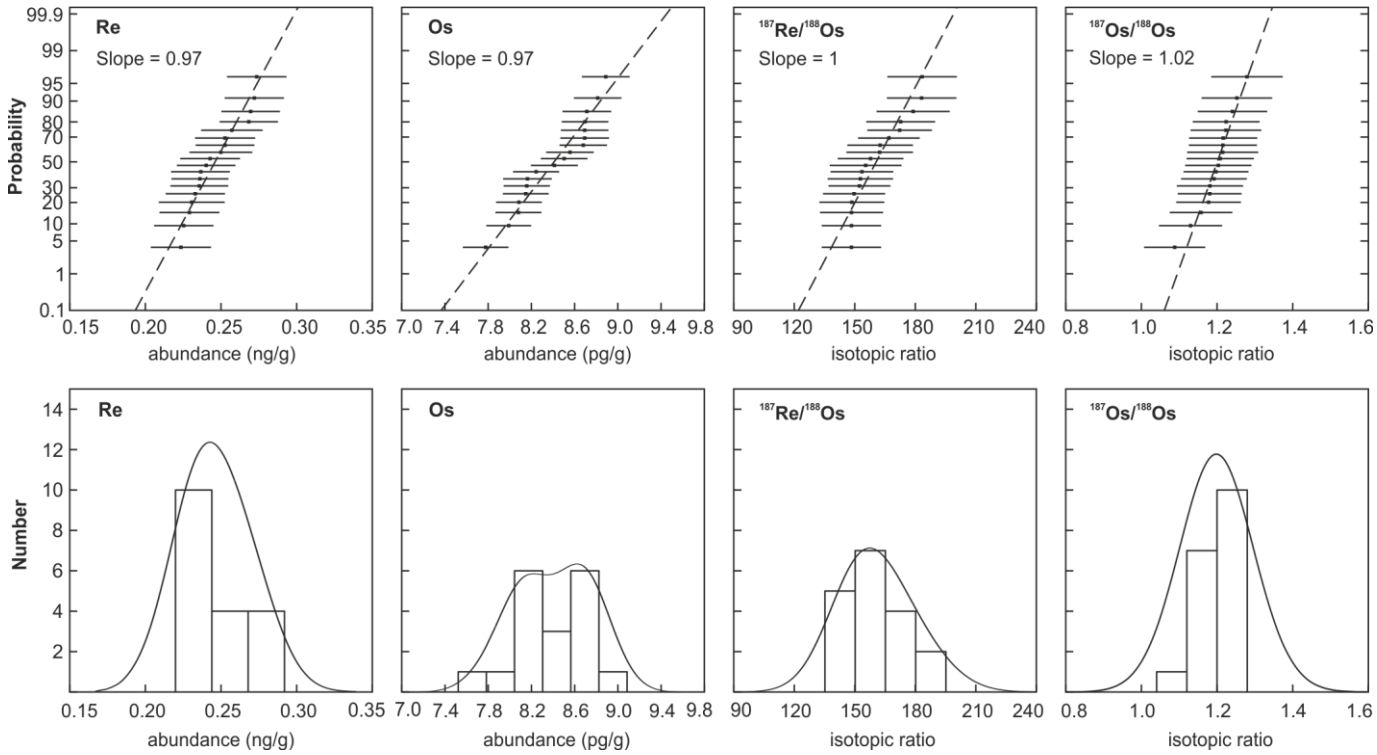


Figure 4 Comparison of the Re and Os mass fractions of RM 8505 whole oil, asphaltene and maltene. Data-point error ellipses are the 2 *s* level combined measurement uncertainties of the measurement process.

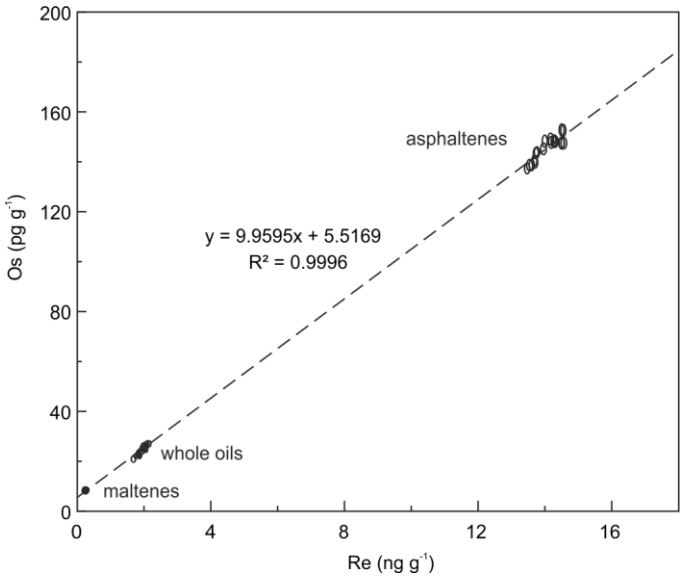


Figure 5 Comparison of the Re-Os isotopic compositions of the RM 8505 whole oil, asphaltene and maltene. Data-point error ellipses are the 2 *s* level combined measurement uncertainties of the measurement process. Regression of the Re-Os data of the whole oil, asphaltene and maltene fractions yields a date of 62.7 ± 5.7 Ma (initial $^{187}Os/^{188}Os$ = 1.030 ± 0.051, MSWD = 0.31). We note that this date value likely does not bear any geological meaning in regard to the timing of oil generation of Venezuelan petroleum systems (see text for discussion).

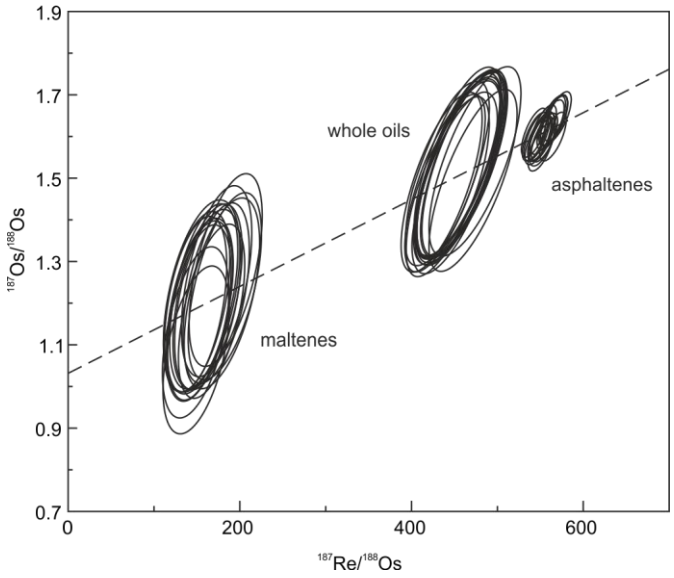
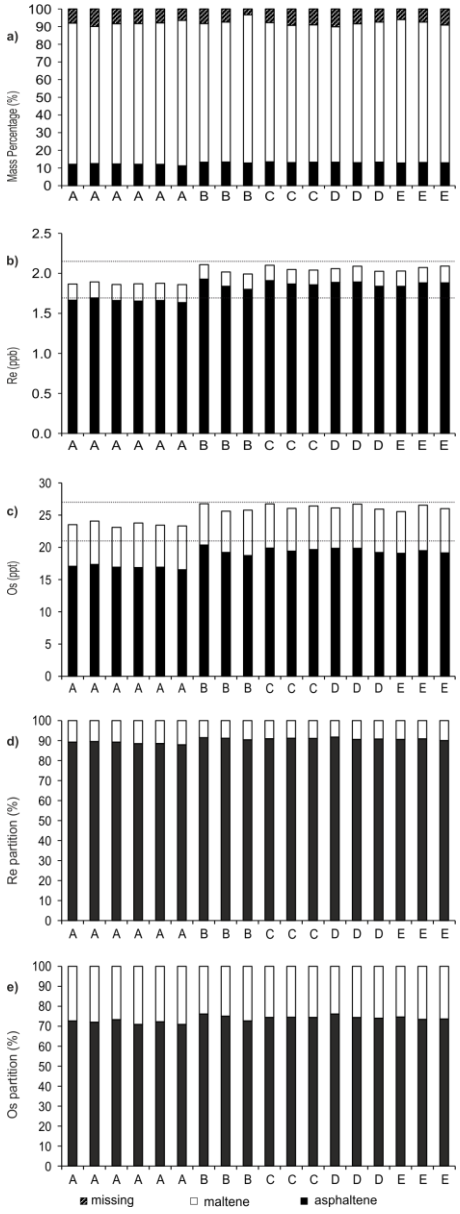


Figure 6 Mass balance of asphaltene-maltene separation and Re-Os budget of RM 8505 oil: a) mass percentages of asphaltene and maltene; b) Re budget of RM 8505 oil separated asphaltene and maltene fractions, i.e. $Total\ Re = asphaltene\ Re\ abundances \times asphaltene\ mass\ fraction + maltene\ Re\ abundances \times maltene\ mass\ fraction$; c) Os budget of RM 8505 oil separated asphaltene and maltene fractions, i.e. $Total\ Os = asphaltene\ Os\ abundances \times asphaltene\ mass\ fraction + maltene\ Os\ abundances \times maltene\ mass\ fraction$; d) Re percentages of asphaltene and maltene within oil, e.g. $maltene\ Re\ abundances \times maltene\ mass\ fraction/Total\ Re$ and e) Os percentages of asphaltene and maltene within oil, e.g. $(maltene\ Os\ abundances \times maltene\ mass\ fraction)\ /\ (Total\ Os)$. See text for discussion.


a)
Mass Percentage (%)
b)
Re (ppb)
c)
Os (ppt)
d)
Re partition (%)
e)
Os partition (%)
A A A A A A B B B C C C D D D E E E
missing
maltene
asphaltene

752

753

Figure 7 Comparison of the Re-Os isotopic compositions of asphaltene, crude oil and maltene of previously studied oils: a) seven oils from Selby *et al*. (2007) and b) selected data of three oils from Georgiev *et al*. (2016). Both studies utilized *n*-heptane for the separation although with slightly different protocols. See text for discussion.

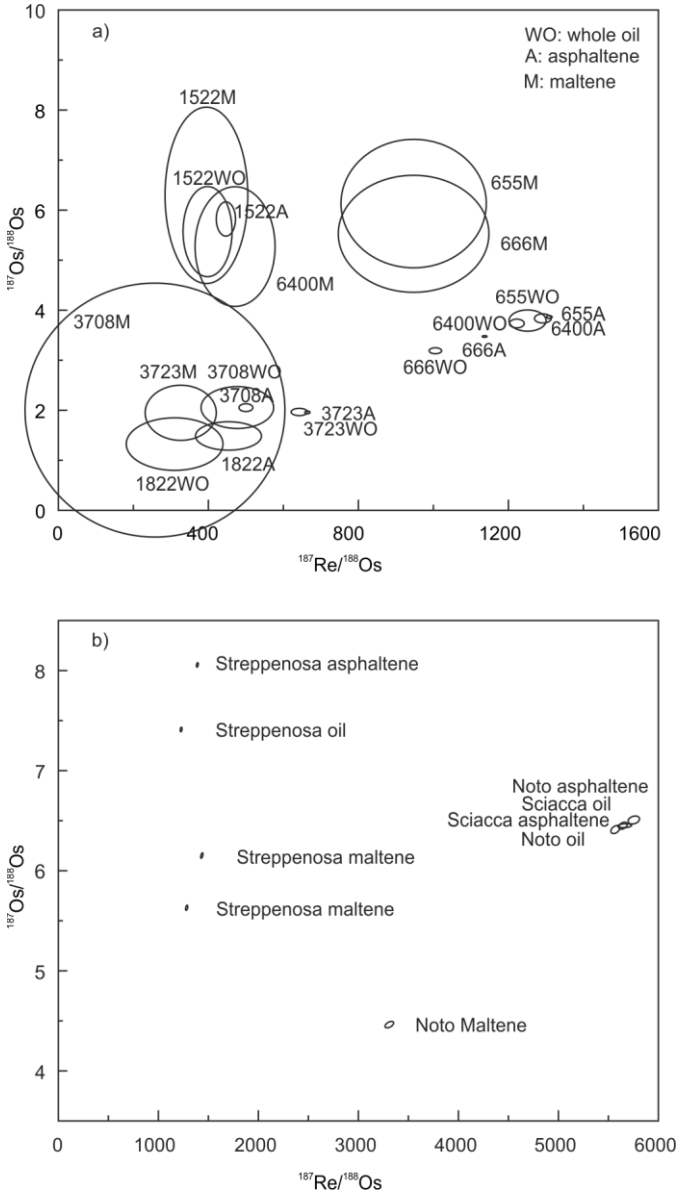


Figure 8 Linearized probability plots (top) and histograms and probability density curves (bottom) of the homogenised asphaltene Re-Os data. The Os data represents the total Os mass fraction. The linearized probability data points are plotted using the 1 *s* level combined measurement uncertainties of the measurement process (see Table 5).